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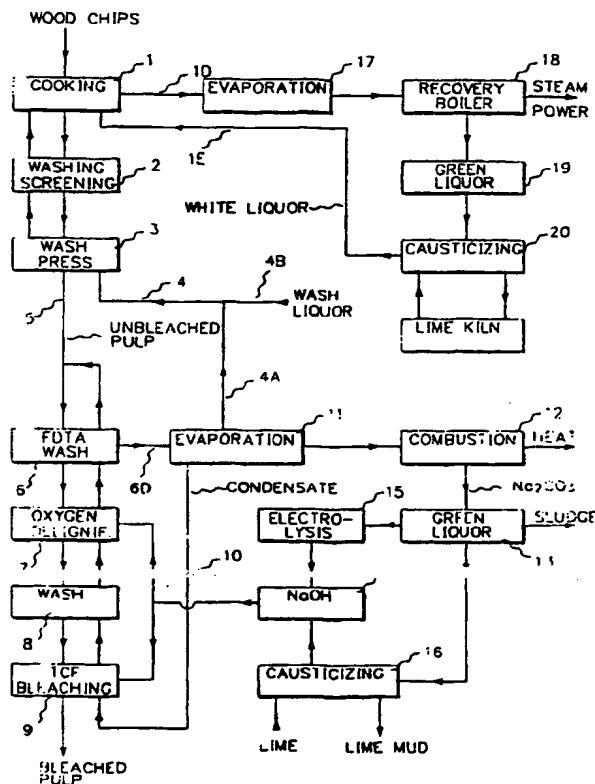
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(54) Title: METHOD OF BLEACHING PULP WITHOUT USING CHLORINE-CONTAINING CHEMICALS

## (57) Abstract

The present invention relates to a process for producing pulp which is cooked under alkaline conditions and which is bleached without using chlorine-containing bleaching chemicals, in which process used cooking chemicals are recovered in a first recovery installation (18) and used bleaching chemicals are recovered in a second recovery installation (12), and, preferably, these bleaching chemicals are regenerated, wholly or in part, and reused in an oxygen-delignification stage (7) and/or in a TCF bleaching stage (9).



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Method of bleaching pulp without using chlorine-  
containing chemicals  
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5    Technical field

          The present invention relates to a process for  
producing pulp which is cooked under alkaline  
conditions and which is bleached without using  
10 chlorine-containing bleaching chemicals, with separate  
installations being used for recovering and for incin-  
erating/gasifying filtrates from the cooking and the  
bleaching, respectively.

15   Background and problems

          Bleaching pulp without using chlorine-  
containing chemicals provides processing solutions  
which are of great interest from the environmental  
20 point of view. Thus, the discharge of impurities into  
the bleaching plant effluent can be reduced  
substantially and, in the optimum case, virtually  
eliminated by, in an appropriate manner, collecting up  
and concentrating the organic and inorganic compounds  
25 in the effluent and subsequently incinerating together  
the concentrates and the used chemicals from the  
cooking procedure. A process of this type has been  
reported in Swedish Patent Application no. 9201477-8.

          Bleaching without chlorine-containing chemicals  
30 is carried out using hydrogen peroxide, sodium  
hydroxide and ozone, in particular. These bleaching  
chemicals are expensive, so that bleaching costs are  
significantly higher than in the case of conventional  
bleaching using chlorine and chlorine dioxide. It is  
35 therefore desirable, if possible, to be able to recover  
the bleaching chemicals, especially sodium hydroxide,  
separately. Sodium hydroxide is principally obtained in  
association with preparing chlorine gas by the

electrolysis of sodium chloride. With decreasing use of chlorine gas, there is some risk of sodium hydroxide becoming an item in short supply.

The process, which is advantageous from the environmental point of view, of returning the used bleaching chemicals, and organic material released during the bleaching, to the system for recovering cooking chemicals can give rise to problems under certain circumstances. If the quantity of sodium compounds and sulphur-containing compounds in the bleaching plant effluent exceeds the requirement for "make-up" chemicals to cover losses, an imbalance arises in the Na/S ratio in the recovery cycle for cooking chemicals. This can lead to problems of having too high an emission of sulphur to the environment, and to other disturbances of the process as well. Another problem, which is equally serious in many works, can be that organic material in the bleaching plant effluent, which is incinerated in the works recovery boiler, leads to overloading of the boiler. A works recovery boiler is often utilized to maximum capacity. Overloading therefore results in the production of pulp having to be decreased, which is an economic disadvantage. In those instances where transfer of used bleaching chemicals to the recovery cycle for cooking chemicals can lead to imbalance in the Na/S ratio and/or overloading of an existing recovery boiler, a separate recovery cycle for the bleaching chemicals would be highly advantageous.

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#### Solution and advantages

In accordance with the process which is indicated in Patent Claim 1, this invention provides a solution, which is technically and economically advantageous, both to the requirement for recovering bleaching chemicals separately and to the problems of limited capacity in the recovery boiler. In the

35

following, the term bleaching also embraces oxygen delignification.

#### Brief description of the figures

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The invention will be described below with reference to the enclosed figures, in which:

Fig. 1 shows a block diagram of a preferred embodiment in principle according to the invention, and  
10 Fig. 2 shows a preferred installation for its realization.

#### Detailed description

15 Figure 1 shows an embodiment of the invention in the form of a block diagram of a sulphate works in which the bleaching is totally chlorine-free (henceforth termed TCF). Wood chippings are cooked in a digester house 1 which is equipped for modified  
20 sulphate cooking and which permits delignification to low kappa numbers. Subsequently, the pulp is washed and screened 2. After the screening 2, there follows a further washing stage 3. A preferred form of the invention is that the final washing stage for  
25 unbleached pulp consists of a washing press 3, or another press, which permits dehydration to a high dry matter content. The washing liquid 4 for the final washing stage 3 consists of chemically purified water 4B and/or evaporation condensate 4A. The unbleached  
30 pulp 5 is thus thoroughly washed.

After the washing, and any intermediate storage, the pulp is pumped to an acid wash stage 6, which includes the possible addition of a chelating agent, for example EDTA. The purpose of this stage is  
35 to remove heavy metals. Filtrate from a suitable stage in the TCF bleaching plant 9 and, where appropriate, recirculated filtrate from the wash 6 after the acid wash stage 6 are used for adjusting the consistency of

the pulp. After the acidification, the pulp is washed in a washing system possessing a high degree of washing efficacy. The washing liquid for the wash of the acid wash stage consists of a suitable filtrate from the subsequent oxygen-delignification stage 7 or the TCF bleaching plant 9.

After the acid wash stage, there follows an oxygen-delignification stage 7. In the oxygen stage, delignification takes place to a low kappa number which, for soft wood, is lower than 15, preferably lower than 12, and for hard wood is lower than 12, preferably lower than 10.

The treatment of the pulp with acid and, where appropriate, with chelating agent prior to the oxygen stage 7 removes heavy metal ions which otherwise impair selectivity during the oxygen delignification, i.e. cause degradation of the cellulose. This wash thus permits the delignification to be taken further, which is a major advantage for subsequent TCF bleaching.

After the oxygen-delignification stage, the pulp is washed and then conveyed to the TCF bleaching plant 9. The latter can be designed with a number of different sequences, for example one or more peroxide stages (P), peroxide followed by ozone (PZ), peroxide, ozone and peroxide (PZP), or Z(EOP)P, i.e. ozone, alkali extraction in the presence of oxygen and, where appropriate, peroxide, and subsequently a peroxide stage.

Heavy metals, which are harmful for both the peroxide stage and the ozone stage, have already been removed in the acid wash stage 6 prior to the oxygen stage 7. It is not therefore necessary, as is done in conventional peroxide bleaching, for example in the Lignox process (SE-B-466061), to treat the pulp with chelating agent immediately prior to the peroxide stage.

Washing liquid, preferably in the form of evaporation condensate 10, is supplied to one of the

stages in the TCF bleaching plant. Except for the filtrate from the ozone stage, the filtrates from the different stages are in the main conveyed in a counter current fashion to the pulp and drawn off via the wash after the acid wash stage 6. This filtrate contains organic material released from the pulp both in the oxygen stage 7 and in the TCF bleaching plant 9, and used bleaching chemicals, principally sodium compounds arising from added sodium hydroxide and possibly sulphur compounds as well, for example derived from sulphuric acid used for pH adjustment. In addition, the filtrate will contain washing losses from the final washing stage for unbleached pulp in the form of organic material, sodium compounds, sulphides and relatively small quantities of heavy metals, which are derived originally from the wood and possibly bound in complex form.

The filtrate from the acid wash stage 6 is conveyed to an evaporation stage 11, where it is evaporated to a high dry matter content. The evaporation 11 can be carried out in a conventional manner in a multi-step evaporation system with steam heating or by so-called mechanical steam compression, by combinations of mechanical steam compression and evaporation with steam, or by evaporation with the aid of low-grade waste heat in the form of hot water or another heat source. Preferably, the same heat-source (e.g. steam) is used for evaporation of the filtrate from the bleaching as for the spent liquor, whereby preferably the filtrate from the bleaching is pre-evaporated in one or two units in the end (seen from the steam flow) of the line of evaporation units and the spent liquor is pre-evaporated in one or two in-between units and preferably thereafter joining the two liquid flows for common evaporation (one, two or three units) in the beginning of the line. Alternatively, the two pre-evaporated liquids are finally evaporated in separate units, whereby at least the remaining heat

(e.g. steam) from the final evaporation of the spent liquor is used for the pre-evaporation and preferably also the remaining heat from the final evaporation of the bleach-effluent is used by joining it with the heat from the final evaporation of the spent liquor. The condensate 4A, 10, which is obtained during the evaporation, can be utilized as a washing liquid in the TCF bleaching plant and/or for washing the unbleached pulp.

10           The concentrated filtrate containing organic material and sodium compounds, and possibly sulphur compounds as well, is conveyed to a separate incineration oven/gasification reactor 12, where the organic material is completely or partially oxidized and the sodium compounds are converted in the main to sodium carbonate and, in the appropriate case, to sodium sulphate or sodium sulphide. The oxidation can either be carried out in the presence of an excess of oxygen or in the presence of a deficiency of oxygen, in which latter case the oxidation takes place under reducing conditions. The latter method, which is more preferably carried out in a CHEMREC<sup>®</sup> reactor, involves gasification of the organic material to form a mixture of carbon monoxide, hydrogen gas and carbon dioxide. The incineration or gasification temperature must be sufficiently high to convert essentially all the carbon to gaseous products and sodium carbonate. Under reducing conditions, sodium sulphide is formed from the sulphur compounds which are supplied.

30           The sodium salts which are formed during incineration are removed in the form of a smelt, which is dissolved in water and forms so-called green liquor 13. During gasification, an aqueous solution of these salts (green liquor) is obtained by direct liquid cooling of the incineration gases, preferably in a so-called quench system. The incineration heat can be utilized for generating steam and/or preparing hot water. The combustible gases, principally hydrogen gas,

carbon monoxide and methane, which are formed during the gasification represent a flexible energy source. The carbon monoxide gas which is formed can, by means of the so-called shift reaction, be used for generating  
5 further hydrogen gas. The crude hydrogen gas obtained in this way can be purified and used together with oxygen gas for the local preparation of hydrogen peroxide.

The green liquor 13 is filtered carefully in  
10 order to separate off precipitated substances which are contrary to the process, such as heavy metals and other impurities. It is then utilized in whole or in part for preparing sodium hydroxide 14. This can be carried out either by electrolysis 15 or by so-called  
15 causticization 16. In the latter case, slaked lime is added, which reacts with the sodium carbonate to give sparingly soluble calcium carbonate and sodium hydroxide. The calcium carbonate (lime sludge) is separated off by filtering and conveyed to a lime kiln  
20 for re incineration.

Sodium hydroxide, obtained either by the electrolysis of green liquor or alternatively by causticization, is used as a bleaching chemical in the oxygen-delignification stage 7 and/or for regulating  
25 the pH in a peroxide stage (P) or an alkali extraction stage (E) in the TCF bleaching plant 9. The system thus becomes to a large extent self-supporting with regard to sodium hydroxide, which is economically advantageous. In addition, the system is almost  
30 entirely closed, with the discharges of organic material and other impurities in the effluent water having in the main been eliminated.

Oxygen, which can also be prepared within the works, is required in addition to the above mentioned  
35 chemicals.

The upper part of the block diagram in Figure 1 shows how the spent liquor (the filtrate from the cooking) is conveyed to an evaporation installation 17 in

which the spent liquor is evaporated, in order, subsequently, to be incinerated in a recovery boiler 18. The heat which is produced in the recovery boiler is conserved in the form of steam, whose energy content is subsequently converted, for example into electric power. In the recovery boiler 18, the inorganic products contained in the spent liquor form a smelt consisting, in the main, of sodium carbonate and sodium sulphide which are collected from the recovery boiler and dissolved in water in order to form green liquor 19. The green liquor is then converted in a causticization installation 20 such that new cooking liquid, i.e. white liquor ( $\text{NaOH} + \text{Na}_2\text{S}$ ), is formed which is returned to the digester 1.

Sodium sulphate is obtained during the supra-stoichiometric incineration of bleaching plant effluents which contain sulphur-containing compounds. The green liquor produced under these circumstances will therefore contain both sodium carbonate and sodium sulphate. Causticization of the green liquor results in the formation of calcium sulphate, which, however, is relatively soluble as compared with the calcium carbonate (lime sludge). The sodium hydroxide solution will therefore contain a relatively high content of sulphate ions. In addition, the lime consumption will increase and the lime sludge will contain a relatively high content of calcium sulphate, which can interfere with the course of the lime cycle. These difficulties can be avoided by using an organic acid, for example oxalic acid or acetic acid, for adjusting the pH in the acid bleaching stages. The organic acid is incinerated in the boiler and does not interfere with the causticization reaction. Organic acids can, naturally, also be used in systems which are based on the gasification of concentrates of bleaching plant effluents, and in this way the problems with sulphur can be eliminated completely.

When a green liquor containing both sodium

carbonate and sodium sulphate is electrolyzed, sulphuric acid and sodium hydroxide are obtained. These chemicals can be separated by means of a suitable membrane and subsequently recirculated independently to the bleaching plant.

Sulphur compounds contained in the mother liquor give rise, in the main, to sodium sulphide, rather than sodium sulphate, when partial incineration under reducing conditions, i.e. gasification, takes place. However, an aqueous solution of sodium sulphide can be oxidized with oxygen, under pressure and at elevated temperature, to sodium sulphate, and the mixture with sodium carbonate subsequently subjected to electrolysis in accordance with the above description.

Any necessary "make-up" to compensate for losses of chemicals in the recovery cycle of the bleaching plant can be supplied in the form of fresh NaOH and, where appropriate, sulphuric acid,  $H_2SO_4$ . Chemical surpluses and any necessary regulation of the enriched concentration of substances which are contrary to the process and which derive originally from the wood can take place either by transferring a part of the green liquor or residual solution from the electrolysis to the system for recovering cooking chemicals for regulating the pH of the effluent water of the works. In the first-mentioned case, most of the impurities, for example heavy metals, are removed by way of the green liquor sludge which is obtained on filtering the green liquor, and then dealt with in a manner which is advantageous from the environmental point of view.

Figure 2 shows an embodiment of the invention in the form of a system solution for the fibre line. Soft wood chippings are steamed 1A and preimpregnated 1B and then cooked in a KAMYR<sup>®</sup> digester 1C equipped for modified sulphate cooking, which permits delignification to low kappa numbers, 18-22, while preserving strength properties. The pulp, which has

been partially washed in this process, is washed further firstly in a diffuser 2A and after screening 2B on a filter 3A which functions as a combined thickener and washing apparatus. Subsequently, the pulp is washed and thickened on a washing press 3B to the pulp consistency of 25-35%. Chemically purified water 4B or evaporation condensate 4A is used as the washing liquid. The washing liquid is conveyed in counter current to the digester, where it moves upwards, again in counter current, to the withdrawal screen, where black liquor 1D is drawn off and conducted to evaporation 17 and thence to incineration in a recovery boiler 18 (see Figure 1). The smelt from the boiler is dissolved in water to form green liquor containing mainly sodium carbonate and sodium sulphide. The green liquor is subsequently causticized in a known manner to form white liquor containing mainly sodium hydroxide and sodium sulphide. The white liquor 1E is conveyed to the digester for decomposing the wood chippings.

The pulp leaves the washing press with a consistency of 25-35%. It is well washed and contains only about 3 kg of  $\text{Na}^+$ /ton of pulp and about 10 kg of dissolved organic material. In addition, the pulp contains relatively small quantities of heavy metals.

The pulp from the washing press 3B is then diluted to a consistency of about 10% with filtrate, in the proportion of about 6 tons/ton of pulp, from the ozone stage (Z) wash in the subsequent TCF bleaching plant 9. Using a KAMYR<sup>®</sup> MC pump 6A, acid, for example organic acid or sulphuric acid, is added together with a chelating agent such that a pH of 5-6 is achieved. The temperature in the EDTA stage 6B or Q stage should be 50-90°C and the dwell time 30-60 minutes.

The pulp treated in this way is subsequently washed in a washing apparatus 6C (included in the so-called acid washing stage 6) possessing a high degree of washing efficacy, at least 80%, preferably 90-95%, measured as its effect in separating off manganese. In

the preferred case, a KAMYR<sup>®</sup> two-stage diffuser 6C is employed. Other washing devices, for example a washing press or one or more washing filters in series, may be employed. During the washing, the pulp is freed from heavy metals, which are to be found in the form of complexes in the filtrate 6D, which is conveyed to separate evaporation 11, (see Fig. 1) oxidation and chemical recovery. The filtrate 6D also contains most of the organic material which was released in the oxygen-delignification stage 7 and the TCF bleaching 9. In addition, most of the sodium compounds, and, where appropriate, the sulphur compounds which were added to the bleaching are to be found in the filtrate. -

NaOH, at the rate of 10-20 kg per ton of pulp, and, where appropriate, magnesium salt, are supplied in an MC pump 7a to the pulp, which is well washed and freed from heavy metals, and the pulp is then conveyed under pressure via an MC mixer 7B, in which oxygen and, where appropriate, steam are supplied, to a reactor 7C having a dwell time of about 30-90 minutes, preferably of about 60 minutes. The temperature of the pulp is 80-110°C and the pressure 3-10 bar. During the oxygen delignification, the kappa number is lowered to less than 15, preferably less than 12. The residual chemicals and released organic material are washed out after the oxygen stage in one or more washing devices 8 having a degree of washing efficacy of 80-95%, preferably 90-95%. Figure 2 shows a KAMYR<sup>®</sup> two-stage diffuser 8, but the washing can also be carried out using other devices having a similar degree of washing efficacy, for example filters or washing presses.

Hydrogen peroxide, at the rate of 10-35 kg of H<sub>2</sub>O<sub>2</sub>/ton of pulp, preferably 20-30 kg of H<sub>2</sub>O<sub>2</sub>/ton of pulp and sodium hydroxide, at the rate of 5-30 kg of NaOH/ton of pulp, preferably 15-25 kg of NaOH/ton of pulp, are subsequently supplied to the oxygen-delignified pulp by means of an MC pump 9A and the pulp is then heated to a temperature of 75-95°C, preferably

of 80-90°C. After that, the pulp is conveyed to one or more reaction towers having a dwell time of 3-8 hours, preferably 4-6 hours.

The peroxide-bleached pulp, having a brightness of 75-85 ISO, is washed in a washing apparatus 9C possessing a high degree of washing efficacy, for example in a KAMYR® two-stage diffuser. Either chemically purified water or evaporation condensate 10 is used as the washing liquid. The temperature of the washing liquid should be 35-55°C, preferably 40-50°C. The displaced peroxide-bleaching filtrate 9D is recirculated to the preceding washing apparatus 8, it being possible to utilize both residual peroxide and heat in the peroxide stage.

After the peroxide bleaching stage 9B, the pulp is pumped onwards by means of a KAMYR® MC pump 9E and is acidified to pH 2-6, preferably pH 3-4. Sulphuric acid, for example, or an organic acid, for example oxalic acid or acetic acid, is used for the acidification. Ozone gas in oxygen, at a concentration of 5-15% O<sub>3</sub>, is added at a pressure of 5-12 bar and mixed into the pulp suspension, which has a consistency of about 10%. One or more mixers of the KAMYR® MC mixer 9F type, or another type of efficient mixing apparatus, is/are employed for the admixture. The temperature of the pulp suspension should be 35-55°C, preferably 40-50°C. The charge of ozone gas should be 2-6 kg of O<sub>3</sub>/ton of pulp, preferably 3-5 kg of O<sub>3</sub>/ton of pulp.

After the admixture, the pulp suspension containing ozone gas is conveyed through a reactor 9G having a dwell time of 1-10 minutes, preferably 1-4 minutes. Subsequently, the pressure is lowered in a cyclone device 9H, with the gas being separated from the pulp suspension. The residual gas, which mainly consists of oxygen with small quantities of unreacted ozone, is cleaned of fibre in a scrubber (not shown) and conveyed to an ozone-destroying apparatus. The oxygen gas can be compressed in a compressor and reused

in the oxygen-delignification stage, for example.

The pulp suspension, which has been freed of gas, is pumped to a washing stage 9i, for example a KAMYR® one-stage diffuser. If appropriate, sodium hydroxide, for neutralizing to pH5-10, and sulphur dioxide, for eliminating remaining ozone in the pulp suspension, are added before the wash. After the washing stage, alkali and hydrogen peroxide are supplied in a KAMYR® MC pump and/or mixer 9J. The charge of peroxide should correspond to 1-5 kg of H<sub>2</sub>O<sub>2</sub> per ton of pulp and the charge of alkali should be sufficiently high to adjust the pH to pH 10-11. The temperature of the peroxide stage 9K must be 50-80°C, preferably 60-75°C, and the dwell time of the pulp 1-4 hours, preferably 2-3 hours.

After the peroxide stage 9K, the pulp is washed in a KAMYR® one-stage diffuser 9L or other washing device having a similar degree of washing efficacy. At this stage, the brightness of the finally bleached pulp is 85-90 ISO, preferably 88-90 ISO.

If sulphuric acid is used in the acid wash stage 6 and the ozone stage 9B, the filtrate 6D, which is withdrawn from the acid wash stage (the Q stage), will have the following approximate composition per ton of pulp:

Organic material	about 75 kg
Na <sup>+</sup>	" 30 kg
SO <sub>4</sub>	" 15 kg
Total dry matter	120 kg

The quantity of liquid is about 10 m<sup>3</sup> per ton of pulp. This corresponds to a dry matter content of about 1.2%. The filtrate is evaporated to a dry matter content of 50-70%, with about 9 tons of condensate being obtained which is used for washing the pulp after the first peroxide stage, or at another suitable point in the process. The evaporated concentrate, which has a calorific value of about 9 MJ/kg of dry matter, is incinerated in an oxidizing environment, a smelt

containing about 22 kg of  $\text{Na}_2\text{SO}_4$  and about 52 kg of  $\text{Na}_2\text{CO}_3$  being formed. The smelt is dissolved in water. The "green liquor" which is obtained is thoroughly filtered in order to separate off solid impurities, for example by precipitating out heavy metal salts. Subsequently, the solution is electrolyzed in electrolyzers having membranes which separate the sodium hydroxide and sulphuric acid which are formed. Based on the chemical content of the green liquor, about 13 kg of sulphuric acid and about 46 kg of NaOH are thus formed at an efficiency of 90%. The necessary requirement for the oxygen-delignification stage and the TCF bleaching is about 15 kg of sulphuric acid per ton of pulp and about 50 kg of NaOH per ton of pulp. The requirement for fresh chemicals is therefore limited to about 2 kg of  $\text{H}_2\text{SO}_4$  and 4 kg of NaOH, in addition to peroxide and oxygen gas.

If an organic acid is used for acidification in the acid wash stage and ozone stage, it is in the main only sodium carbonate which is obtained in the smelt. After dissolution in water, the sodium carbonate solution can be treated with slaked lime, with sodium hydroxide and calcium carbonate (lime sludge) being formed. The latter is washed and transferred to the lime kiln for re-incineration. The sodium hydroxide is used for bleaching.

If there is no economic motivation for recovering sodium hydroxide or sulphuric acid, the salts can be used for other purposes, for example as make-up chemicals in the cooking chemical cycle. In this case, the benefit is obtained that the recovery boiler for the cooking chemical cycle is not loaded with organic material released in the oxygen-delignification stage and/or in the TCF bleaching plant. In addition, discharge of organic material from the bleaching plant is eliminated.

Naturally, the invention can also be used in connection with the production of pulp from hard wood

or other raw material, such as annual plants. The requirement for chemicals will vary depending on the degree of pulp brightness required and on the cellulose-containing raw material which is incorporated. The method can also be used in those cases where the cooking liquid is sulphur-free or has a low sulphur content and is mainly made up, for example, of an alkaline hydroxide. The method can advantageously be employed in those cases where the alkali metal base in the cooking and/or the oxygen delignification and TCF bleaching mainly consists of potassium instead of sodium. It will be evident to the person skilled in the art that the appurtenant incineration/gasification installation 12 can operate in accordance with essentially any of the currently known incineration/gasification principles, even if a CHEMREC® reactor is preferred. In addition, it will be evident that the recovery installation intended for the spent liquor can consist of a gasification reactor, for example a CHEMREC® reactor. Over and above this, it should be pointed out that the invention is not limited to only two recovery boilers/reactors and that it is possible to conceive of combining certain parts in the recovery cycle from the systems illustrated separately in Figure 1. The degree of washing efficacy is defined as follows:

$$\frac{(X-Y)}{X} \times 100;$$
 where X is the quantity of unwanted substance prior to washing and Y is the quantity of the said substance remaining after washing, for a given quantity of pulp. The manganese content is advantageously employed as a reference value for the said substance.

The solitary "A" in Figure 2 indicates the addition of chemically purified water or evaporation condensate.

## Patent Claims

1. Process for producing pulp which is cooked under alkaline conditions and which in the main is bleached without using chlorine-containing bleaching chemicals, characterized in that used cooking chemicals are recovered in a first recovery installation (18) used bleaching chemicals are recovered, wholly or in part, in a second recovery installation (12), which bleaching chemicals are preferably regenerated, wholly or in part, and reused in an oxygen-delignification stage (7) and/or in a TCF bleaching stage (9).
2. Process according to Patent Claim 1, characterized in that prior to an oxygen-delignification stage (7), the unbleached pulp is treated with acid and, where appropriate, with chelating agent and is washed (6), preferably with a degree of washing efficacy of at least 80%, more preferably at least 90%.
3. Process according to Patent Claim 2, characterized in that the greater part of the organic material released in the oxygen-delignification stage (7) and in the TCF bleaching stage (9), and of the bleaching chemicals, which have been supplied and in the main used, is drawn off together with the filtrate (6D) from the said washing stage (6C).
4. Process according to Patent Claim 3, characterized in that the filtrate (6D) which is drawn off is limited to at most 15 tons per ton of pulp, preferably at most 10 tons per ton of pulp, and preferably the content of dry matter in the drawn-off filtrate is concentrated by evaporation to at least 50%, preferably at least 60%.

5. Process according to Patent Claim 4,  
c h a r a c t e r i z e d i n that the concentrated  
filtrate (6D) which is drawn off from the bleaching is  
incinerated in an oxidizing environment under  
5 stoichiometric or suprastoichiometric conditions, and  
the resulting inorganic chemicals are dissolved in  
liquid.

6. Process according to Patent Claim 4,  
10 c h a r a c t e r i z e d i n that the filtrate (6D)  
which is drawn off from the bleaching and concentrated  
is gasified in a reducing environment, most preferably  
in a CHEMREC<sup>®</sup> reactor, and the resulting inorganic  
chemicals are dissolved in liquid.

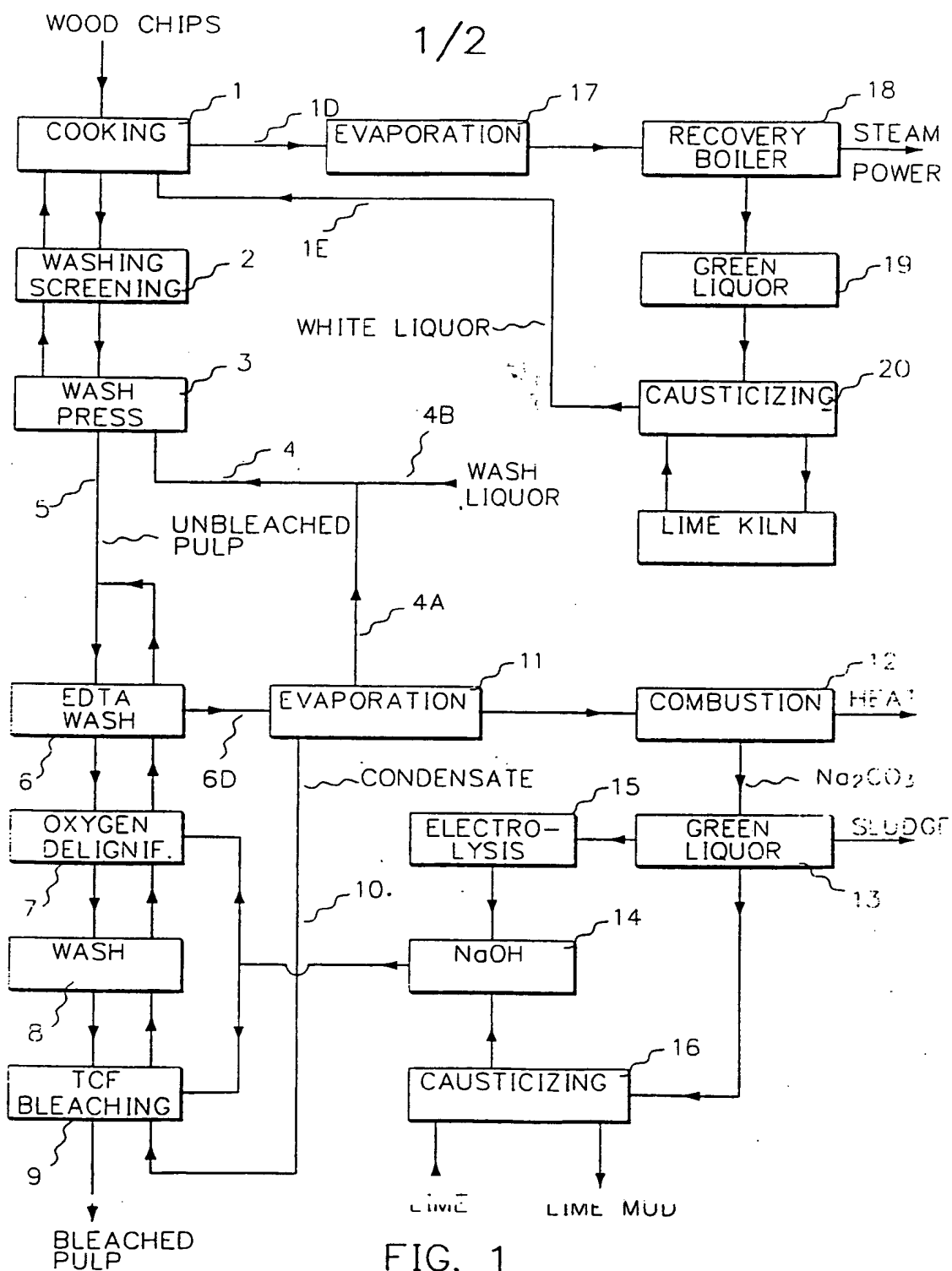
15 7. Process according to Patent Claim 5 or 6,  
c h a r a c t e r i z e d i n that alkali metal  
hydroxide is recovered from the liquid solution by  
causticization or by electrolysis of dissolved alkali  
20 metal carbonate.

8. Process according to Patent Claim 5 or 6,  
c h a r a c t e r i z e d i n that sulphuric acid is  
recovered from the liquid solution by electrolysis of  
25 dissolved alkali metal sulphate.

9. Process according to Patent Claim 6,  
c h a r a c t e r i z e d i n that dissolved sulphide  
obtained by reductive incineration is oxidized with  
30 oxygen to sulphate prior to electrolysis.

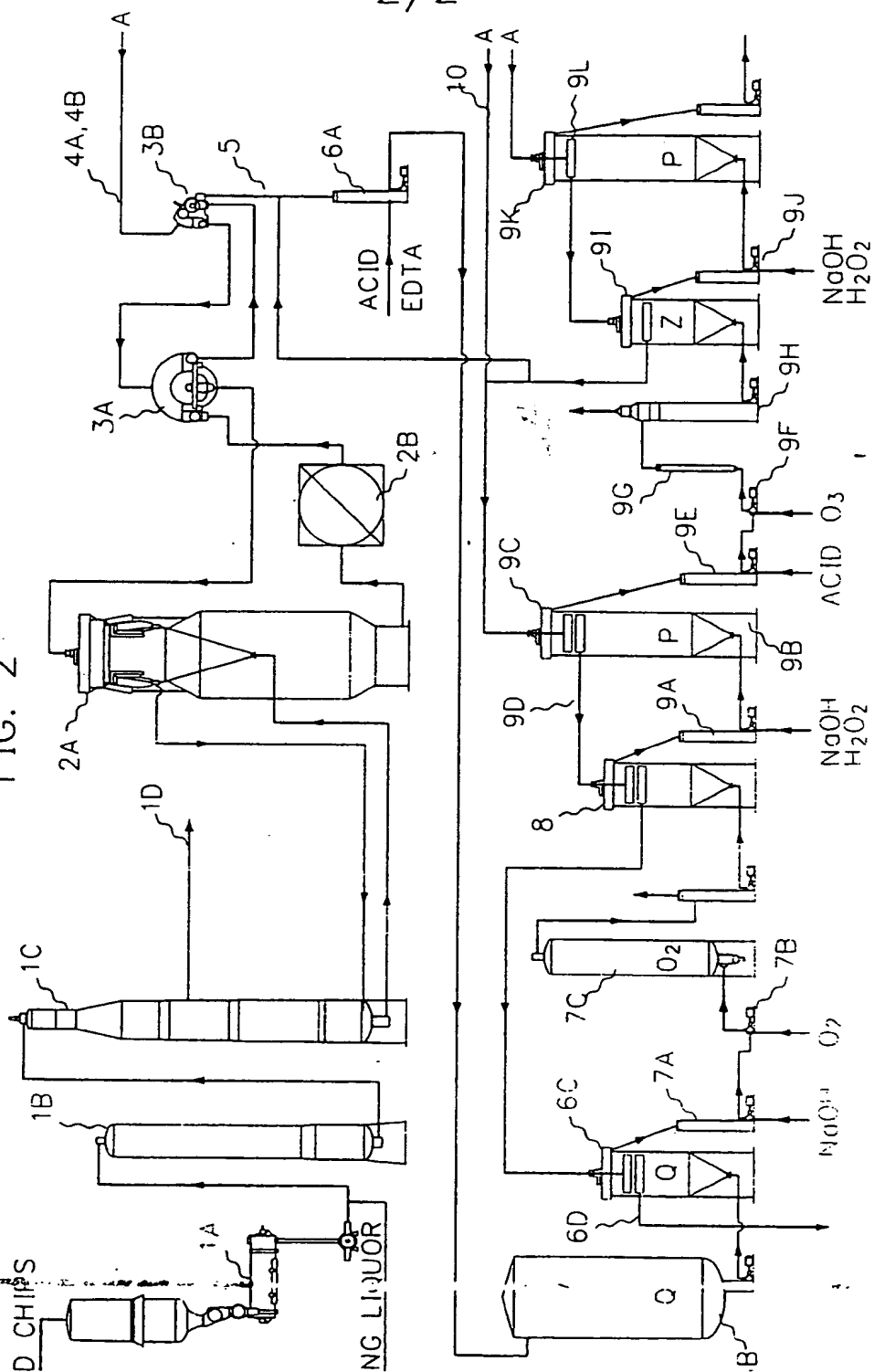
10. Process according to Patent Claims 1 to 7,  
c h a r a c t e r i z e d i n that necessary  
acidification in the acid wash stage (6), with or  
35 without the addition of chelating agent, and any acid  
stages in the TCF bleaching plant (9), are brought  
about by supplying an organic acid.

11. Process according to Patent Claim 1,  
c h a r a c t e r i z e d i n that, the bleach  
effluent and the spent liquor are evaporated by using  
mainly the same heat source.



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FIG. 2



## A. CLASSIFICATION OF SUBJECT MATTER

IPC5: D21C 9/00, D21C 11/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5164043 (BRUCE F. GRIGGS ET AL), 17 November 1992 (17.11.92)  --	1
A	US, A, 5164044 (BRUCE F. GRIGGS ET AL), 17 November 1992 (17.11.92)  -- -----	1

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

11 March 1994

Date of mailing of the international search report

16 -03- 1994

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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

28/01/94

International application No.

PCT/SE 93/00925

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US-A-	5164043	17/11/92	US-A-	5164044	17/11/92
			US-A-	5188708	23/02/93
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US-A-	5164044	17/11/92	US-A-	5164043	17/11/92
			US-A-	5188708	23/02/93
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